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MINERALOGICAL CHARACTERIZATION OF TWO ALUNITE AND TWO NATROJAROSITE SAMPLES

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May 1987

Project: 3.0.77.01
Silver Recovery in the Zinc Industry

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25 pp

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 87-75 (TR)

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MINERALOGICAL CHARACTERIZATION OF TWO ALUNITE AND TWO NATROJAROSITE SAMPLES

by

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ABSTRACT

Two alunite and two natrojarosite samples were characterized chemically and mineralogically to determine their general suitability for solubility measurements. Alunite from Marysvale, Utah, was found to be relatively pure and close to end-member alunite in composition. Although an alunite from Lake Bracciano, Italy, also was close to end-member alunite in composition, it contained traces of an unidentified contaminant which might adversely affect the solubility determinations. The two natrojarosite samples from Mt. Martha, Victoria, Australia, and Port Addis, New South Wales, Australia, consisted mostly of natrojarosite but with minor amounts of silicates (quartz, muscovite, silica gel) and traces of other contaminants. The natrojarosites occurred both as tiny euhedral crystals and as larger irregular masses. Significant substitution of K for Na and Al for Fe occurred in the natrojarosite structure. Further-

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more, the Na/K and Fe/Al ratios varied widely, and such variations could render both samples unsuitable for accurate solubility measurements from which thermodynamic properties could be calculated.

Key words: alunite; natrojarosite; mineralogical characterization; cation substitutions; SEM-EDX studies.

CARACTERISATION MINERALOGIQUE DE DEUX ECHANTILLONS D'ALUNITE ET DE NATROJAROSITE

par

T.T. Chen* et J.E. Dutrizac*

RESUME

Les auteurs ont effectué la caractérisation chimique et minéralogique de deux échantillons d'alunite et de natrojarosite dans le but de déterminer leur adaptation générale à des mesures de solubilité. L'alunite provenant de Marysvale en Utah, était relativement pure et proche du membre terminal de l'alunite au niveau de sa composition. Bien que l'alunite provenant du Lac Bracciano en Italie soit, elle aussi, proche d'un membre terminal de l'alunite au niveau de sa composition, elle contenait toutefois des traces d'un contaminant non identifié qui pourrait avoir un effet défavorable sur les mesures de solubilité. Les deux échantillons de natrojarosite provenant de Mt. Martha, Victoria, Australie et de Port Addis, New South Wales, Australie étaient composés surtout de natrojarosite avec de petites quantités de silicates (quartz, muscovite, gel de silice et d'autres contaminats en traces. Les natrojarosites se présentent à la fois sous forme de cristaux enédriques et de masses irrégulières plus grandes. Des substitutions importantes de K pour Na et de Al pour Fe se produisent dans la structure de natrojarosite. De plus, les rapports Na/K et Fe/Al variaient de

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beaucoup, et de telles variations pourraient rendre les deux échantillons impropres à servir aux mesures de solubilité à partir des quelles on peut calculer les propriétés thermodynamiques.

Mots-clés: alunite; natrojarosite; caractérisation minéralogique; substitutions de cations; études SEM-EDX

INTRODUCTION

A sound knowledge of the thermodynamic properties of alunite-jarosite compounds is necessary to predict their formation conditions, to understand their behaviour in residue ponds and to estimate the energy required for their thermal decomposition. Although some thermodynamic data are available (1,2,3), these are incomplete and invariably are limited to 25°C. There is a need for confirmatory studies and for an extension of the data to different alunite-jarosite species and to a wider range of conditions. One convenient means of measuring the thermodynamic properties of such compounds is by accurate solubility measurements, and such techniques have been employed in most of the studies reported (1). If the solubility measurements are to be meaningful, then of course, the equilibrating solid phase must be well characterized with respect to its chemical and mineralogical compositions. This is especially important for the jarosite-type compounds where extensive cation substitutions are known to occur (4) in both natural and synthetic compounds.

Recently, Dr. C.G. Clifton of Oregon State University has been conducting solubility measurements on alunite-jarosite group minerals with the aim of using this information to generate thermodynamic data over a range of temperatures. Because Dr. Clifton lacks the facilities for the detailed characterization of his equilibrating solid phases, he requested that such

characterization be conducted at CANMET. As this type of work is directly relevant to CANMET's own studies and because such an investigation would extend the range of reference samples available to CANMET, a chemical and mineralogical study was undertaken to characterize the two alunite ($KAl_3(SO_4)_2(OH)_6$) and two natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) samples provided by Dr. Clifton. The results of those studies are presented in this report.

EXPERIMENTAL

The four samples were provided in powder form and were from the following localities:

1 - Alunite, Lake Bracciano, Italy, Australian Museum sample D-8955, Sydney.

2 - Alunite, Marysvale, Utah, U.S.A., Australian Museum sample (no number), Sydney.

3 - Natrojarosite, Mt. Martha, Victoria, Australia, National Museum of Australia sample M21990, Melbourne.

4 - Natrojarosite, Port Addis, New South Wales, Australia, Australian Museum sample D-36417, Sydney.

The four samples were examined in the as-received state and without drying.

In addition to classical chemical analysis of the samples, the solids fractions were examined by a variety of mineralogical techniques. The samples were studied by both

Debye-Scherrer and Guinier-deWolff X-ray diffraction analyses using filtered Co K_α radiation (λ=1.7889 Å). Some of the fractions were analyzed with a Rigaku X-ray powder diffractometer with a rotating anode and using filtered Cu K_α radiation (λ=1.5418 Å). Polished sections of the samples were prepared, and these were examined using ore microscopy, scanning electron microscopy (SEM) and electron microprobe analysis. The principal mineral consituents and coarse grained phases were easily detectable using ore microscopy. The fine grained jarosite particles were examined in detail using the SEM with an energy dispersive X-ray analyser (EDX). Some of the grains also were analyzed with a JEOL 733 electron microprobe, and the data were corrected using standard ZAF correction programs.

RESULTS AND DISCUSSION

The results of the various X-ray diffraction studies done on the four samples are presented in Table 1. The Rigaku diffractometer showed the alunite samples to be "alunite", and there was close agreement of both the intensities and the 2θ values between these samples and the PDF alunite standard. The diffractometer also showed the two natrojarosite samples to be mostly "natrojarosite" although some line shifts and intensity differences relative to the natrojarosite standard were observed. Experience suggests that such differences could be due to cation substitution effects. More sensitive Guinier-deWolff X-ray diffraction indicated only alunite in the

Marysvale sample, but detected a trace of an unknown constituent (an Al-oxide ?) in the Lake Bracciano sample. Both natrojarosite samples were shown to contain significant amounts of quartz.

Table 1 - X-ray diffraction study of the alunite and natrojarosite samples.

Sample	Rigaku	Guinier-deWolff
Alunite, Lake Bracciano	Alunite	Alunite + trace unknown (Al-oxide ?)
Alunite, Marysvale	Alunite	Alunite
Natrojarosite, Mt. Martha	Natrojarosite	Natrojarosite + quartz
Natrojarosite, Port Addis	Natrojarosite + trace quartz	Natrojarosite + quartz

Chemical analysis of the as-received samples was carried out, and the results are presented in Table 2. Lead and calcium also were analyzed, but were <0.02% in all the samples. Both alunites, and especially the Marysvale sample, are relatively pure and contain only minor substitutions of Na for K and Fe for Al. The amount of acid insoluble material is negligible. The calculated formula for the Lake Bracciano sample is $(K_{0.81}Na_{0.19})Al_{3.10}(SO_4)_{2.00}(OH)_6$, and the minor substitution of

Na for K in this sample is apparent. The corresponding formula for the Marysvale sample is $(K_{0.96}Na_{0.06})Al_{3.09}(SO_4)_{2.00}(OH)_6$. Consistent with the X-ray diffraction data (Table 1) is the high acid insoluble content of the two natrojarosite samples. The X-ray diffraction data suggest that a major part of the insoluble fraction is quartz, but other phases also are present as will be seen below. As is often the case for natural jarosites, there is a modest substitution of Al for Fe that generally is greater than the substitution of Fe for Al in the alunites. The high K content of the natrojarosites also is evident, and this is a reflection of the significant stability of (potassium) jarosite (4). Sodium exceeds potassium, however, and both samples are correctly described as "natrojarosite".

The analytical results for the two natrojarosites were corrected for the acid insoluble contents, and the resulting analytical data are given in Table 3. Both formulae indicate ~15 atomic % potassium substitution for sodium and a modest Al substitution for Fe. Some hydronium (H_3O^+) substitution for Na also seems to occur (5), but the amounts are not large (3-5 mol%).

Because of the purity and near-stoichiometric composition of the alunites, and especially the Marysvale sample, further work was not done on these materials. Additional mineralogical studies, however, were carried out on the two natrojarosites. Microscopic study using SEM-EDX techniques

Table 2 - Chemical compositions of the as-received alunite and natrojarosite samples; wt%.

Sample	Na	K	Fe	Al	SO_4	Insol
Alunite, Lake Bracciano	1.06	7.62	0.04	20.05	46.20	0.32
Alunite, Marysvale	0.34	9.09	0.03	20.28	46.74	0.14
Natrojarosite Mt. Martha	3.44	1.19	30.91	0.55	36.61	6.78
Natrojarosite Port Addis	3.60	1.16	31.22	0.20	36.67	6.82
Alunite, Theoretical	0.00	9.31	0.00	19.26	45.72	0.00
Natrojarosite, Theoretical	4.68	0.00	34.14	0.00	39.15	0.00

Table 3 - Analytical data for the two natrojarosites after correction for the insoluble content; wt%.

Sample	Na	K	Fe	Al	SO_4	Formula
Natrojarosite Mt. Martha	3.69	1.27	33.16	0.59	39.27	$(Na_{0.79}K_{0.16}H_3O_{0.05})(Fe_{2.90}Al_{0.10})(SO_4)_2(OH)_6$
Natrojarosite Port Addis	3.86	1.24	33.50	0.21	39.35	$(Na_{0.82}K_{0.15}H_3O_{0.03})(Fe_{2.93}Al_{0.04})(SO_4)_2(OH)_6$

showed the Mt. Martha material to consist of tiny (2 μm) euhedral crystals of natrojarosite (Fig. 1). SEM-EDX study showed a significant K variation among the individual natrojarosite grains, with the larger crystals (rarely 10-20 μm) being more K-rich. Silicon also was detected in the natrojarosite grains, and this is probably due to finely admixed quartz, silica gel, etc. A number of large natrojarosite agglomerates also was observed (Fig. 2, large central grains), and these are clearly inhomogeneous. The agglomerates are relatively rich in potassium, but seem to have less Si than the tiny euhedral natrojarosite crystals (Fig. 1). The agglomerates represent large numbers of tiny natrojarosite grains stuck together, but the agglomerating agent is not known. In addition to natrojarosite, many irregular quartz (or silica gel) particles also were observed, and the particle sizes of the quartz varied widely.
Several large lath-like particles of muscovite (mica group) also were observed, and Figure 3 illustrates such a particle surrounded by tiny euhedral natrojarosite crystals. The basal cleavage of the muscovite is readily apparent in the photomicrograph. From a solubility point of view, none of the impurity phases present are likely to interfere with the measured concentrations of Na, K, Fe, Al or SO_4.

Corresponding SEM-EDX study of the Port Addis sample showed this material to be even more complex than its Mt. Martha counterpart. Figure 4 presents a general view of this sample that consists of both isolated euhedral natrojarosite crystals

as well as large natrojarosite agglomerates. Even at the magnification used, it is clear that the natrojarosites are compositionally inhomogeneous and/or contain significant numbers of fine inclusions. The average natrojarosite particle size is much larger than that of the Mt. Martha sample. A large number of quartz particles were observed, and several are present (dark grey) in the upper-left corner of Figure 4. Also detected were trace amounts of TiO_2 and Ti-Fe oxide, likely ilmenite. None of the impurity phases are likely to affect adversely the solubility measurements.

Figure 5 shows one of the natrojarosite agglomerates in more detail, and it is clear that these particles consist of both well-formed natrojarosite crystals and irregular natrojarosite masses. The dark areas within the agglomerate reflect either silicate inclusions (black or dark grey) or K-deficient areas. Large variations in the potassium content of the natrojarosite were observed during EDX study of the agglomerated particles. Figure 6 shows several of the euhedral natrojarosite crystals present in the Port Addis sample. The crystals are relatively large ($\sim$20 μm) and are often extremely well developed. Significant compositional variations are evident within individual particles, and many of the individual crystals contain fine silicate inclusions. Often the outer parts of the crystals are potassium-rich (white). The cores of most of the crystals show complex

compositional gradations, and all the crystals indicated wide variations in the Na/K ratio. Persistent traces of Si were detected even within the individual crystals, and presumably this indicates tiny silicate inclusions.

Electron microprobe analysis of the natrojarosite is greatly complicated by the small individual particle sizes (Fig. 1) and by the ubiquitous presence of fine silicate inclusions and major compositional variations (Fig. 5 and Fig. 6). Even with the use of a finely focussed electron beam, the beam-affected region is relatively large, and the results are invariably biased by inclusions or by regions of slightly different composition. A further problem is related to the analysis of sodium. Sodium is relatively insensitive to electron beam analysis and, furthermore, migrates rapidly under the beam. This problem normally is resolved by expanding the electron beam, but this procedure is not possible with such fine grained and heterogeneous samples. As a result, the electron microprobe analyses of the Mt. Martha natrojarosite presented in Table 4 and the Port Addis natrojarosite given in Table 5 should be viewed with some caution. In particular, the Si contents likely originate from associated silicate inclusions and the Na contents are significantly low. Nevertheless, the data are useful in reflecting the general compositions and the compositional variations of K and Al.

Given that the analytical totals were low because

Table 4 - Electron microprobe analyses of the natrojarosite from Mt. Martha; wt%.

Grain No.	Na	K	Fe	Al	Si	SO_4
1	1.1	0.80	32.3	0.07	0.14	37.1
2	2.3	1.2	32.2	0.15	0.25	37.2
3	2.6	1.3	33.9	0.20	0.46	36.1
4	2.3	1.5	33.7	0.16	0.26	37.0
5	1.5	1.1	32.4	0.11	0.14	37.0
6	1.7	1.2	32.6	0.09	0.09	38.3
7	1.5	0.90	32.1	0.08	0.05	36.9
8	1.5	1.1	32.8	0.05	n.d.	36.6
9	2.8	2.8	31.7	0.23	0.65	37.1
10	1.3	3.4	32.8	0.26	0.61	36.4
11	1.5	2.4	33.1	0.17	0.23	37.4
12	1.6	2.6	31.4	0.36	1.1	35.4
13	2.0	0.88	32.5	0.14	0.25	39.6
14	2.3	0.98	33.3	0.22	0.36	37.1
15	2.1	2.8	32.5	0.16	0.22	34.4
Average	1.9	1.7	32.6	0.16	0.32	36.9
Natrojarosite	4.68	0.00	34.14	0.00	0.00	39.15

Table 5 - Electron microprobe analyses of the natrojarosite from Port Addis; wt%.

Grain No.	Na	K	Fe	Al	Si	SO_4
1	1.2	1.1	36.6	0.29	2.6	34.3
2	0.90	2.7	32.4	0.09	0.38	36.9
3	1.1	0.71	32.5	0.08	0.28	36.0
4	0.75	2.7	32.1	0.04	0.27	36.4
5	0.29	0.31	32.4	0.04	0.08	39.0
6	0.76	0.82	32.7	0.05	0.17	36.7
7	1.1	0.41	32.3	0.09	0.46	38.4
7a	0.43	0.48	30.2	0.16	2.3	38.6
8	1.2	1.1	32.1	0.06	0.26	38.6
9	1.7	1.0	31.6	0.09	0.53	37.9
10	1.3	0.43	32.1	0.04	0.12	37.6
11	0.39	1.6	32.0	n.d.	n.d.	37.8
12	1.1	2.2	30.8	0.04	0.19	37.0
13	0.59	2.4	31.5	0.09	1.1	38.7
14	1.1	0.35	31.2	0.04	0.22	38.3
15	0.31	2.4	31.3	0.12	1.1	38.5
16	2.0	0.51	32.0	0.13	2.0	35.8
17	0.60	0.35	32.7	n.d.	0.05	38.5
18	2.2	0.71	31.7	0.31	1.7	34.8
19	0.75	0.80	31.6	0.10	0.69	38.9
20	0.65	1.8	30.8	0.11	0.18	38.6
21	1.3	0.68	31.8	n.d.	0.05	39.2
Average	0.99	1.2	32.0	0.09	0.67	37.6
Natrojarosite	4.68	0.00	34.14	0.00	0.00	39.15

of the small particle sizes involved, both the Fe and SO_4 contents are satisfactorily near to the expected values of natrojarosite. Aluminum replaces Fe^{3+} in the natrojarosite structure, but the amounts of Al substitution are fairly low. The Al contents vary considerably, but such variations, at the given Al concentrations, likely have little effect on the overall solubility of either natrojarosite. The determination of the solubility of Al in the equilibrating solution would, however, have to be made, and cognizance of the presence of Al in the co-existing solid would have to be taken. As noted above, the Na contents are known to be both low and inaccurate; comparison with the analytical data of Table 3 clearly illustrates both points. The K contents, as determined by the electron microprobe, agree fairly well with the analytical data, and the electron microprobe data for this element are felt to be accurate. These data indicate wide variations in the K contents of both natrojarosite samples. For the Mt. Martha natrojarosite, the K contents range from 0.8 to 3.4 wt%; the corresponding range for the Port Addis sample is 0.3 to 2.7 wt%. The presence of large and variable amounts of K substitution for Na is seen as the major difficulty in the use of either sample for solubility studies. Certainly, the K concentrations of the solutions would have to be measured, and the presence of K in the co-existing solids would have to be considered in the thermodynamic calculations. More seriously, however, is the problem of trying to define the composition of the co-existing solid phase. The bulk solubility measurements would not be

representative of single phase material, and it is not clear which composition (lowest K, highest K, average composition, some "special" composition, etc.) would govern the overall solubility. The wide variation of the Na/K ratio is seen as the most serious difficulty in the use of these natrojarosite samples for solubility measurements. The compositional variations observed in this investigation speak strongly in favour of the use of well-prepared synthetic jarosite-type compounds for physico-chemical studies.

CONCLUSIONS

Two alunite and two natrojarosite samples were characterized chemically and mineralogically to determine their general suitability for solubility measurements. Of the four samples studied, only the alunite from Marysvale, Utah, is sufficiently pure and homogeneous to be used confidently for solubility studies. The alunite from Lake Bracciano, Italy, is also relatively pure, but contains traces of an unidentified contaminant which might affect the solubility concentrations. The two natrojarosites, from Mt. Martha and Port Addis, Australia, both contain several percent of siliceous matter, but such silicate compounds should not affect the solubility measurements. Significant substitution of K for Na and Al for Fe was observed in both natrojarosites, and wide variations in the Na/K and Fe/Al ratios were recorded. The presence of large and variable amounts of K is especially significant, and greatly complicates the

solubility measurements. Furthermore, it will be very difficult to define which Na-K jarosite composition determines the solubility.

ACKNOWLEDGEMENTS

The authors are especially appreciative of the efforts of J.H.G. Laflamme for his extensive electron microprobe analyses of the natrojarosite samples. The X-ray diffraction studies were done by P. Carriere and K.M. Besso.

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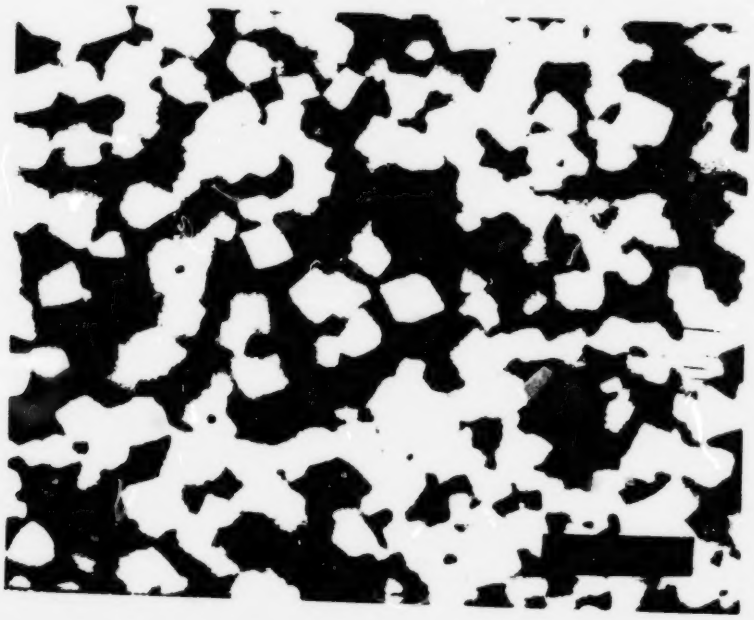

Fig. 1 - SEM micrograph of the euhedral natrojarosite crystals (light grey) which form the majority of the Mt. Martha sample.

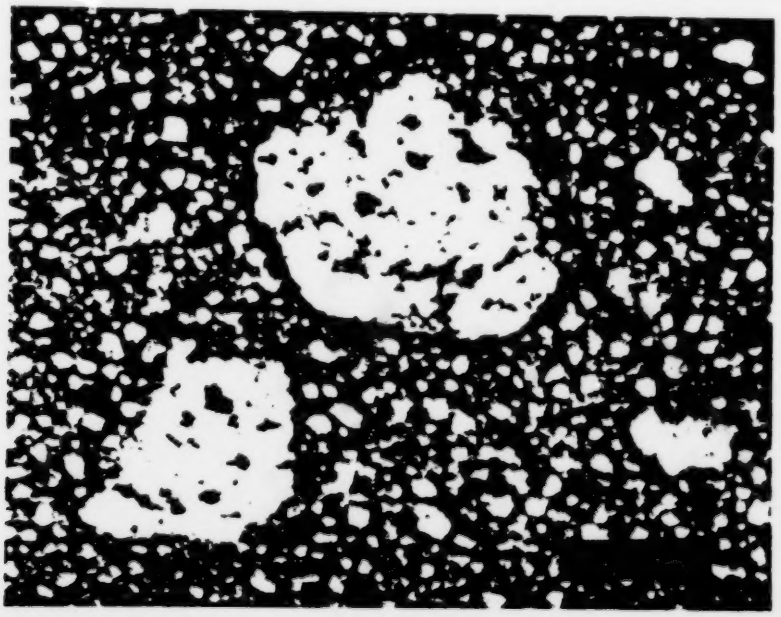

Fig. 2 - SEM micrograph of some large natrojarosite agglomerates (light grey) in the Mt. Martha sample that are relatively K-rich.

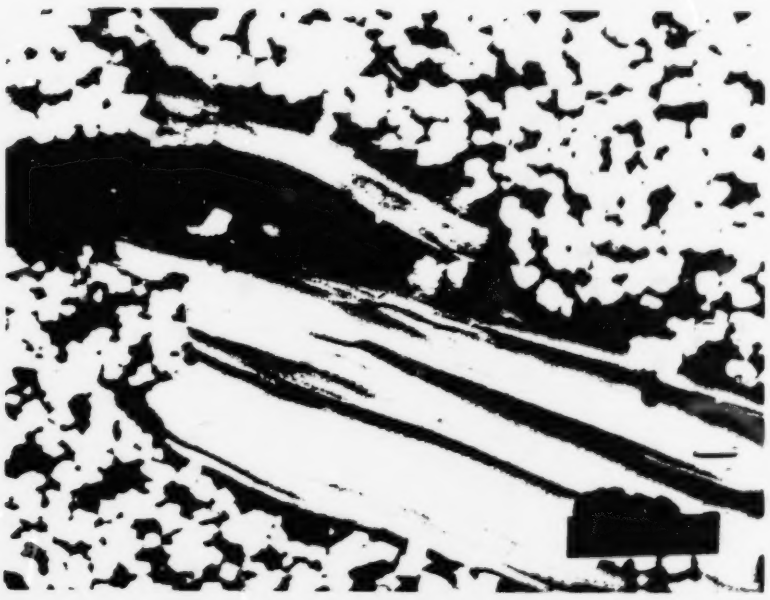

Fig. 3 - SEM micrograph of a large muscovite grain (dark grey) surrounded by euhedral natrojarosite crystals (light grey); Mt. Martha sample.

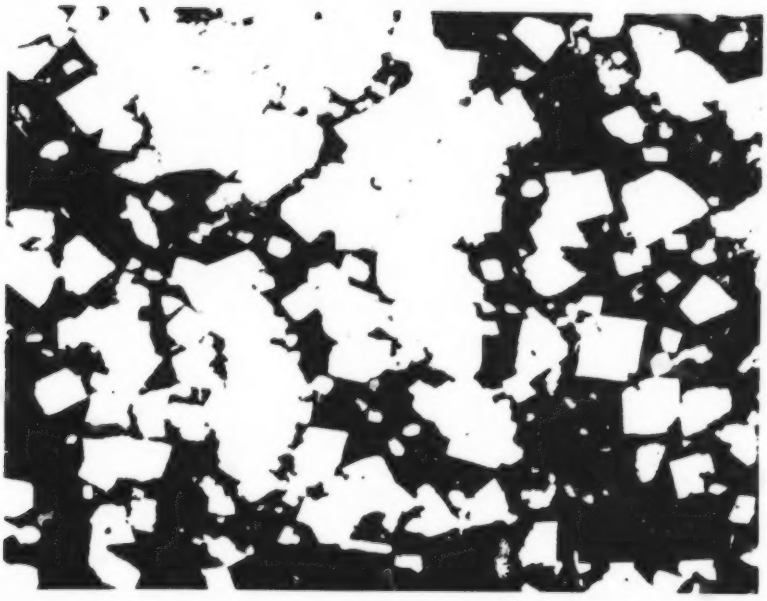

Fig. 4 - SEM micrograph showing the general morphology of the Port Addis sample.

Fig. 5 - SEM micrograph of a natrojarosite agglomerate in the Port Addis sample. The dark grey regions of the agglomerate indicate significant compositional variations.

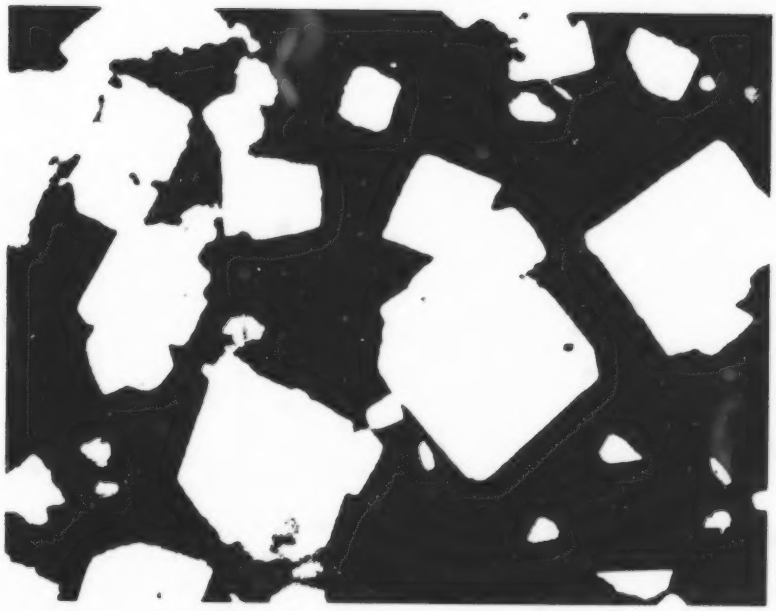

Fig. 6 - SEM micrograph of the euhedral natrojarosite crystals in the Port Addis sample. Darker regions within individual crystals reflect compositional differences.